ESR spectroscopy of catalytic systems - a primer

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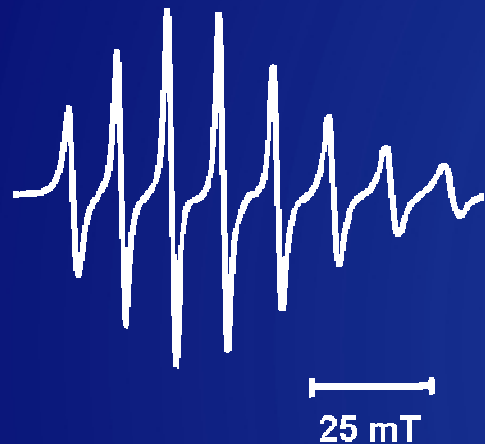
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ESR spectroscopy

Solid vs. solution
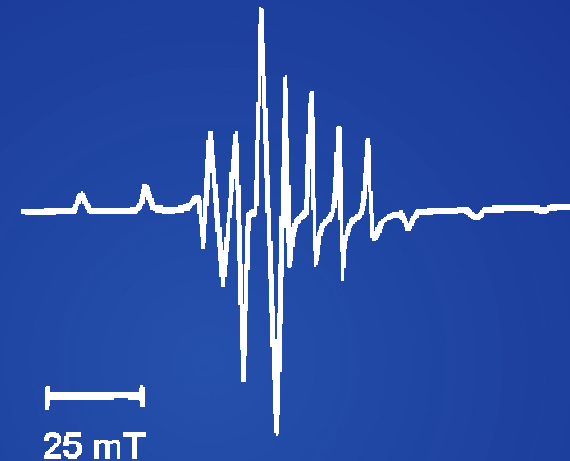
Colloidal solution of nanoparticles
(in water at 300 K)

Colloidal solution of nanoparticles
(in ice at 120 K)

25 mT

25 mT

- What is the nature of the paramagnetic center?
- Which interactions determine the observed spectra?
- Where does the difference between solution and solid come from?

Outline:

- Introduction
- Magnetic interactions of an unpaired electrons

  - Zeeman interaction
  - interactions with other electron spins (group spins and zero field splitting)
  - hyperfine interaction

- relaxation processes

  - in solution
  - in solids
  - magnetic resonance and dynamics

- experimental aspects
- transition metal ions

  - electronic states and spin orbit coupling
  - ions in crystal or ligand fields
  - some examples (Ti^{3+}, VO^{2+} (d^1), Fe^{3+} (d^5), Co^{2+} (d^7), Cu^{2+} (d^9))

- some examples

Introduction
references

ESR spectroscopy

J.A. Weil, J.R. Bolton, J.E. Wertz, *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*, Wiley, New York, 1994.

N.M. Atherton *Principles of Electron Spin Resonance*, Ellis Horwood, New York 1993.

W.Gordy, *Theory and Applications of Electron Spin Resonance*, Wiley, New York, 1980.

A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Dover Publ. 1970.

Practical Aspects

C.P. Poole, *Electron Spin Resonance*, Dover, Mineola, 1996.

Basics of Magnetic Resonance

C. P. Slichter *Principles of Magnetic Resonance*, Springer Series in Solid State Sciences, 3rd Ed., Springer, Berlin, 1996.

R.R. Ernst, G. Bodenhausen and A.Wokaun, *Principles of NMR in one and two Dimensions*, Oxford University Press, Oxford, 1993.

A. Abragam, Principles of Nuclear Magnetic Resonance, Clarendon, Oxford, 1983.
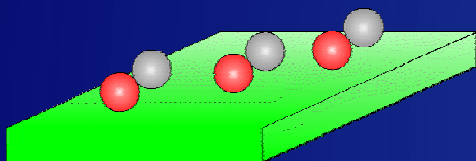
Introduction
What kind of systems?

molecules, complexes:

(diamagnetic)
paramagnetic

metals:
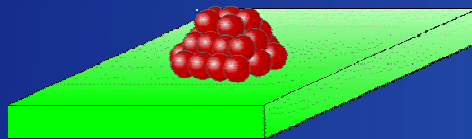
(diamagnetic)
paramagnetic
ferromagnetic
antiferromagnetic

compounds:

(diamagnetic)
paramagnetic
ferromagnetic
antiferromagnetic

radicals: NO, O_2, NO_2

reaction intermediates

transition metal complexes

usually ferromagnetic
metals e.g. Fe, Co, Ni

conduction band ESR
for small particles
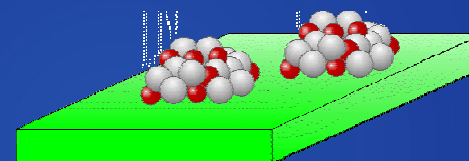
e.g. oxides, nitrides
defects

ESR spectroscopy

Zeeman interaction

Interaction of an angular momentum
with a magnetic field:

classically: $\qquad\qquad E = - \mu \mathbf{B}$

translation to QM $\qquad H = \mu_B \, g \, \mathbf{J} \, \mathbf{B}$
if field is in z-direction: $\qquad H = \mu_B \, g \, J_z \, B_0$

eigenvalues: $\qquad E = \mu_B \, g \, B_0 \, M_J$

for $M_J = \pm 1/2$: $\qquad \Delta E = h\nu = \mu_B \, g \, B_0$

X-band
(~ 9.4 GHz)

Q-band
(~ 35 GHz)

W-band
(~ 94 GHz)

$m_s = \dfrac{1}{2}$

$m_s = -\dfrac{1}{2}$

E

1 $\quad$ 2 $\quad$ 3

B [T]
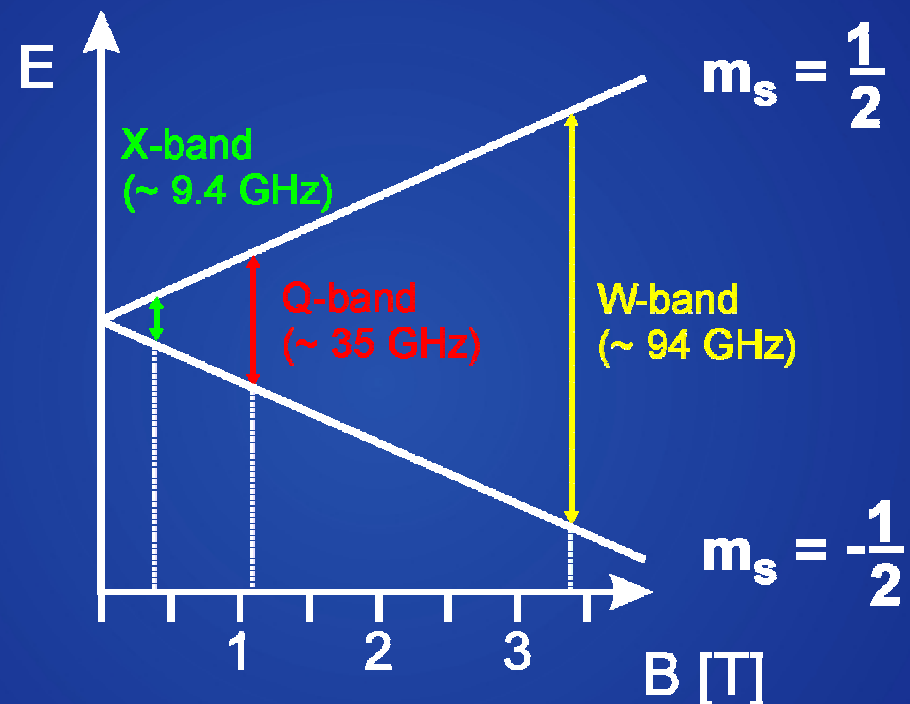
ESR spectroscopy

Zeeman interaction

isotropic case: $\qquad H = \mu_B \, g \, \underline{\mathbf{J}} \, \underline{\mathbf{B}}$

anisotropic case: $\qquad H = \mu_B \, \underline{\mathbf{J}} \, \boldsymbol{g} \, \underline{\mathbf{B}}$

$\qquad$ $\boldsymbol{g}$ is a symmetric (3x3) matrix
$\qquad$ => always possible to diagonalize
$\qquad\qquad$ principal components g_x, g_y, g_z

eigenvalues: $\qquad E = \mu_B \, g_{eff} \, B_0 \, m_J$

with: $\quad g_{eff} = [\, \sin^2(\theta)\,\cos^2(\phi)\,g_x^2 \, +$
$\qquad\qquad\qquad \sin^2(\theta)\,\sin^2(\phi)\,g_y^2 \; +$
$\qquad\qquad\qquad \cos^2(\theta)\,g_z^2\,]^{1/2}$

θ and ϕ describe the orientation of the static magnetic field in the g-matrix coordinate system
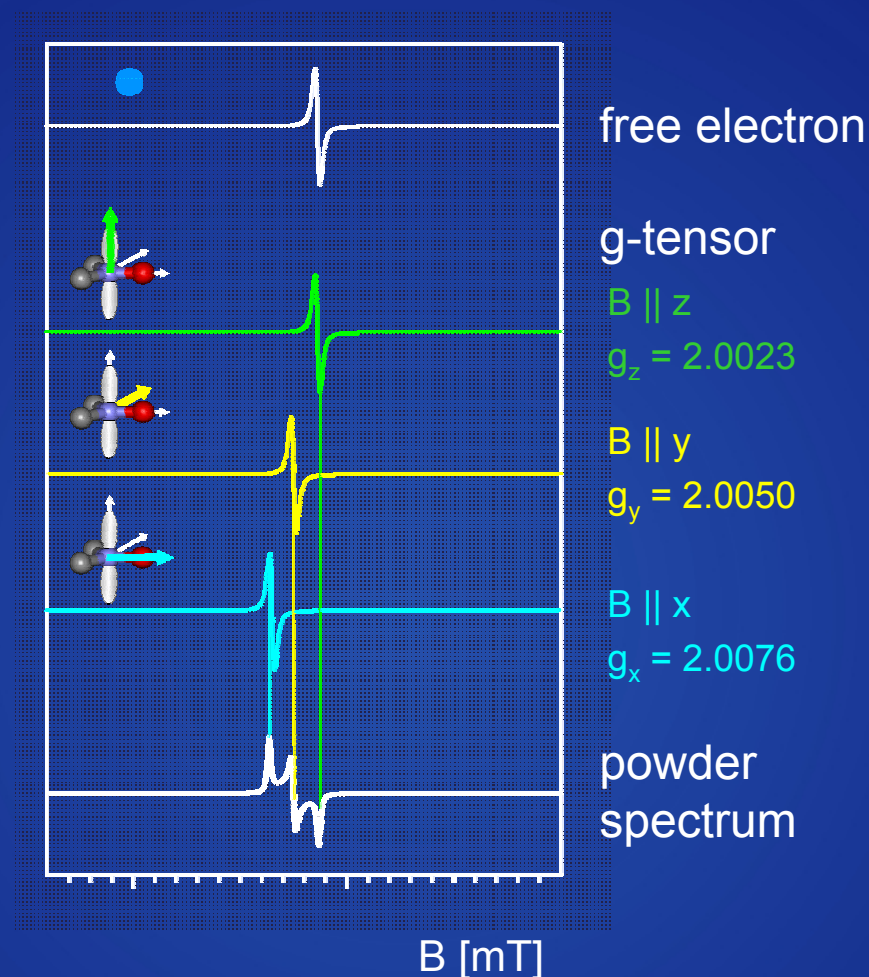
free electron

g-tensor

$B \parallel z$

$g_z = 2.0023$

$B \parallel y$

$g_y = 2.0050$

$B \parallel x$

$g_x = 2.0076$

powder
spectrum

B [mT]

ESR spectroscopy

interactions with other electron spins

1. dipole-dipole interaction (important for distance measurements; X-band 12 Å < r < 60 Å)

$$H_{DD} = \frac{\pi\mu_0}{\hbar} g_j g_i \mu_B^2 \left(\frac{\vec{S}_j \cdot \vec{S}_k}{r_{j,k}^3} - \frac{3(\vec{S}_j \cdot \vec{r}_{j,k})(\vec{S}_k \cdot \vec{r}_{j,k})}{r_{j,k}^5} \right)$$

or in compact form: $H_{dd} = \underline{S}_1 \, \boldsymbol{D} \, \underline{S}_2$

results in splitting of the states which depends on the relative orientation of the interspin axis, the g-matrix coordinate systems, and the orientation of the magnetic field

important special case: $g_j = g_k \approx g_e$ and $E_{zee} > E_{dip}$

$$H_{DD} = \frac{\pi\mu_0}{\hbar} g_j g_i \mu_B^2 \left(\frac{3 \cos^2 \theta - 1}{r_{j,k}^5} \right)$$

average out for integration over a sphere

=> no isotropic contribution

θ = angle between inter-spin axis and magnetic field

ESR spectroscopy

interactions with other electron spins

2. exchange coupling (effective for r < 10 Å)

    two electrons have a certain probability to be found in the same orbital

    extreme case: covalent bond (spin paired => no signal!)

    => ESR is sensitive for weak exchange coupling

    exchange interaction has an isotropic contribution (most of the times this is the only one which is observed)

    $H_{exch} = - J \underline{S}_k \underline{S}_j$

    J negative: spins oriented antiparallel
    antiferromagnetic coupling

    J positve: spins oriented parallel
    ferromagnetic coupling

ESR spectroscopy

group spins and zero field splitting

Hund's rule: more than one energetically degenerate orbital:

first fill one electron in each orbital

$$S = s_1 + s_2 + s_3 = 3/2$$

this results in a total spin S, also called group spin
in short this group spin is often called electron spin S > ½

there is an important consequence:

These system show an interaction which is mediated by the spin orbit interaction and is formally equivalent to the dipole interaction:

$$H_{zfs} = \underline{S}\, D\, \underline{S}$$

the interaction is independent of the field. This is also true for the hyperfine interaction, or the dipolar interaction but the zero field splitting is usually the leading term!

size of the effect can vary dramatically: from small for slightly distorted systems to very large such that no ESR signal can be observed
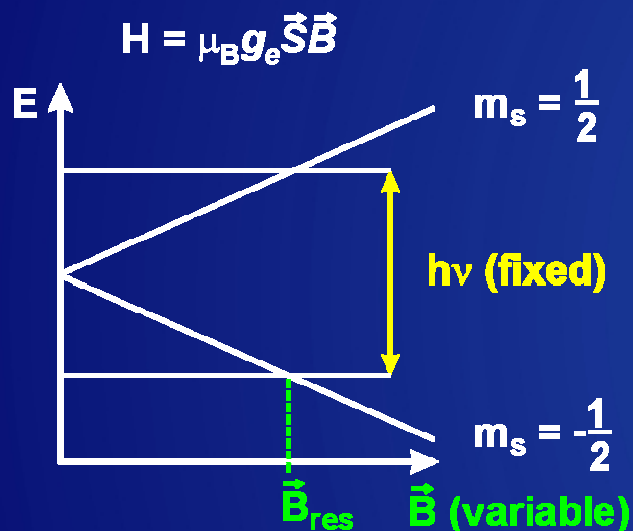
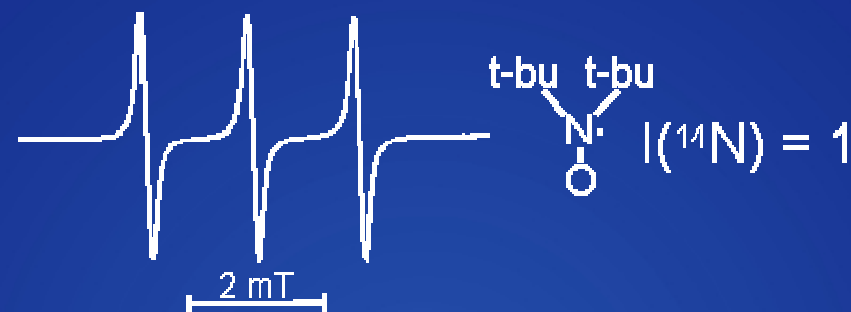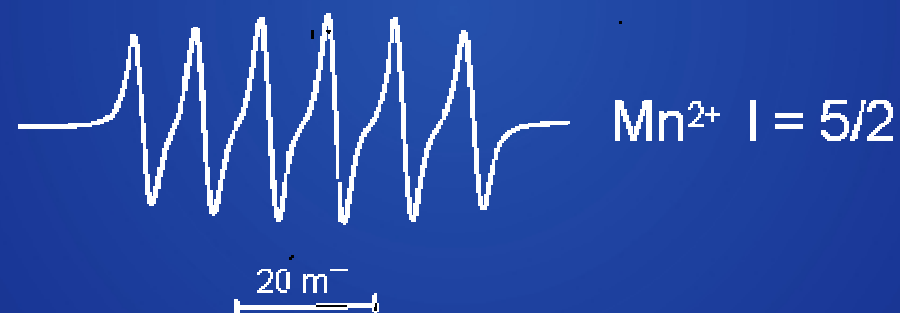# ESR spectroscopy

hyperfine interaction

isotropic case

$$H = \mu_B g_e \vec{S}\vec{B}$$

$m_s = \frac{1}{2}$

$h\nu$ (fixed)

$m_s = -\frac{1}{2}$

$\vec{B}_{res}$ $\vec{B}$ (variable)

DTBN in toluene (300 K)

t-bu t-bu

$I(^{14}N) = 1$

2 mT

MnCl$_2$ in water (300 K)

Mn^{2+} I = 5/2

20 mT

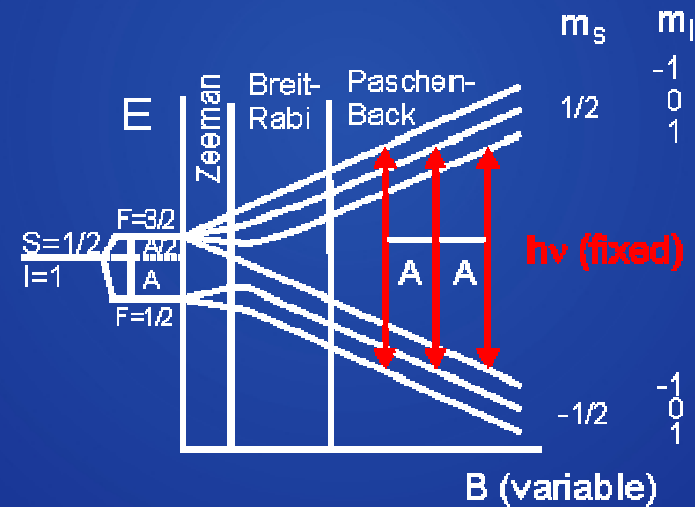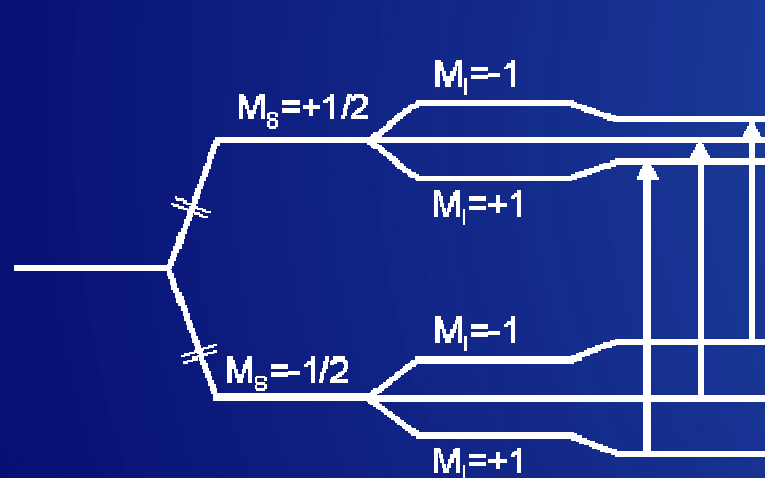reason: hyperfine interaction; (2I+1)-states

ESR spectroscopy

hyperfine interaction

What is hyperfine interaction?

interaction of an electron spin with a nuclear spin

isotropic case

$$H = \mu_B g S_z B_0 - \gamma_n B_0 I_z + a_{iso} I_z S_z$$

el. Zeeman   nuc. Zeeman   hyperfine interaction

ESR spectroscopy

hyperfine interaction

in general: two contributions

1. dipole-dipole interaction:

   $H = \underline{\textbf{S}}\,\textbf{\textit{T}}\,\underline{\textbf{I}}$

   $\textbf{\textit{T}}$ is the anisotropic interaction matrix
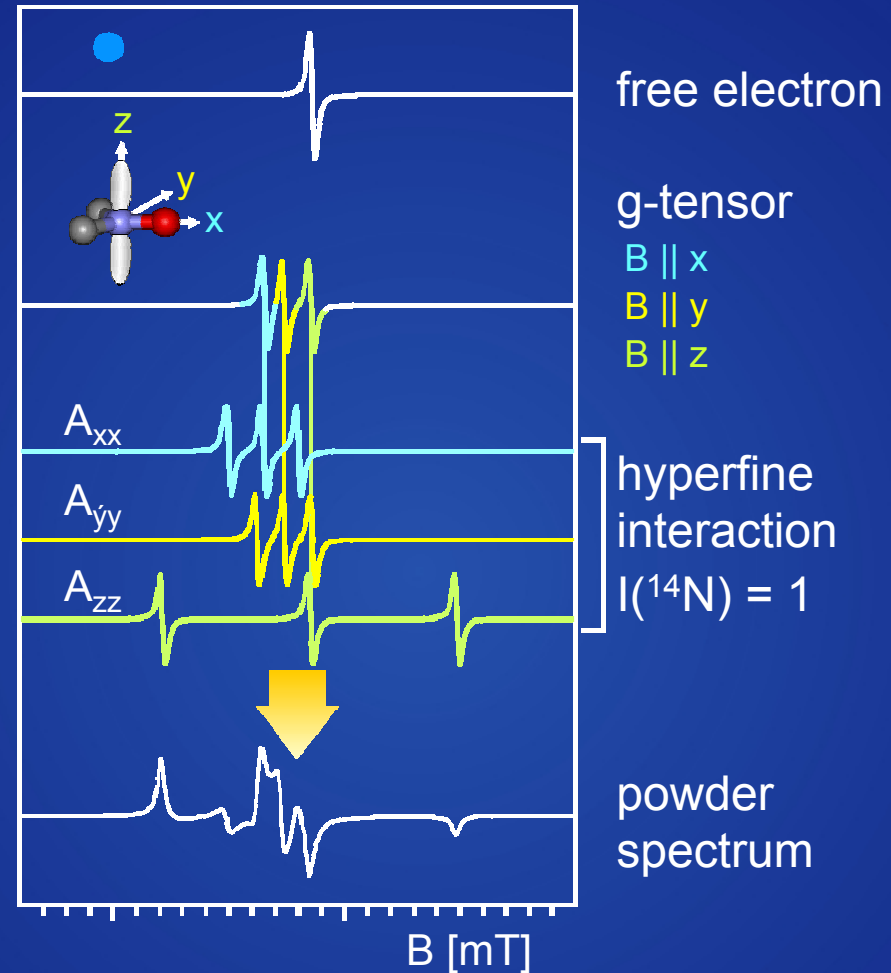   traceless => integral over a sphere vanishes

2. Fermi-contact interaction:

   $H = a_{iso}\,\underline{\textbf{S}}\,\underline{\textbf{I}}$

   isotropic, depend on the probability to find an
   electron at the position nucleus

$H_{hfi} = \underline{\textbf{S}}\,\textbf{\textit{A}}\,\underline{\textbf{I}}$

with $\textbf{\textit{A}} = \textbf{\textit{T}} + a_{iso}\,\textbf{1}$ $\textbf{1}$: unit matrix

free electron

g-tensor
 B || x
 B || y
 B || z

hyperfine
interaction
$I(^{14}N) = 1$

powder
spectrum

B [mT]

A_{xx}

$A_{ýy}$

A_{zz}

ESR spectroscopy

effect of rotational motion

rigid limit

free electron

g-tensor
 B || x
 B || y
 B || z

A_{xx}

A_{yy}

A_{zz}

hyperfine
interaction
$I(^{14}N) = 1$

powder
spectrum

B [mT]

rotational motion

isotropic rotation

$\tau_c > 50$ ns — rigid limit

$\tau_c \approx 15$ ns — slow motion

g_{iso} A_{iso}

$\tau_c < 1$ ns — fast motion
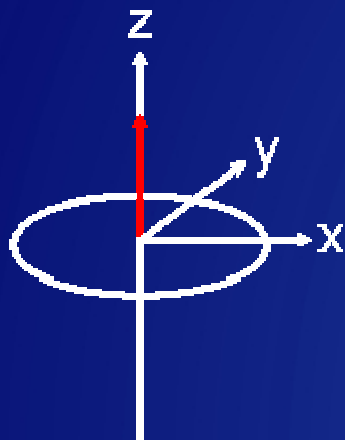
$A_{iso} = 1/3(A_{xx}+A_{yy}+A_{zz})$
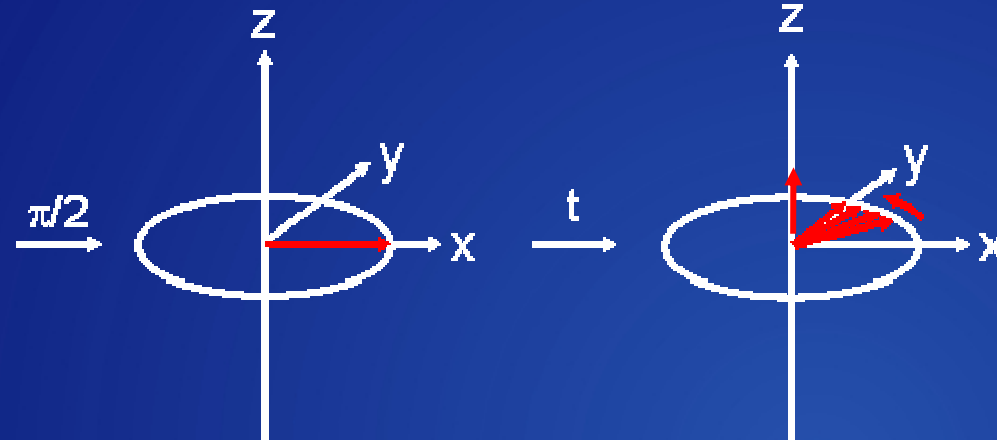
$g_{iso} = 1/3(g_x+g_y+g_z)$
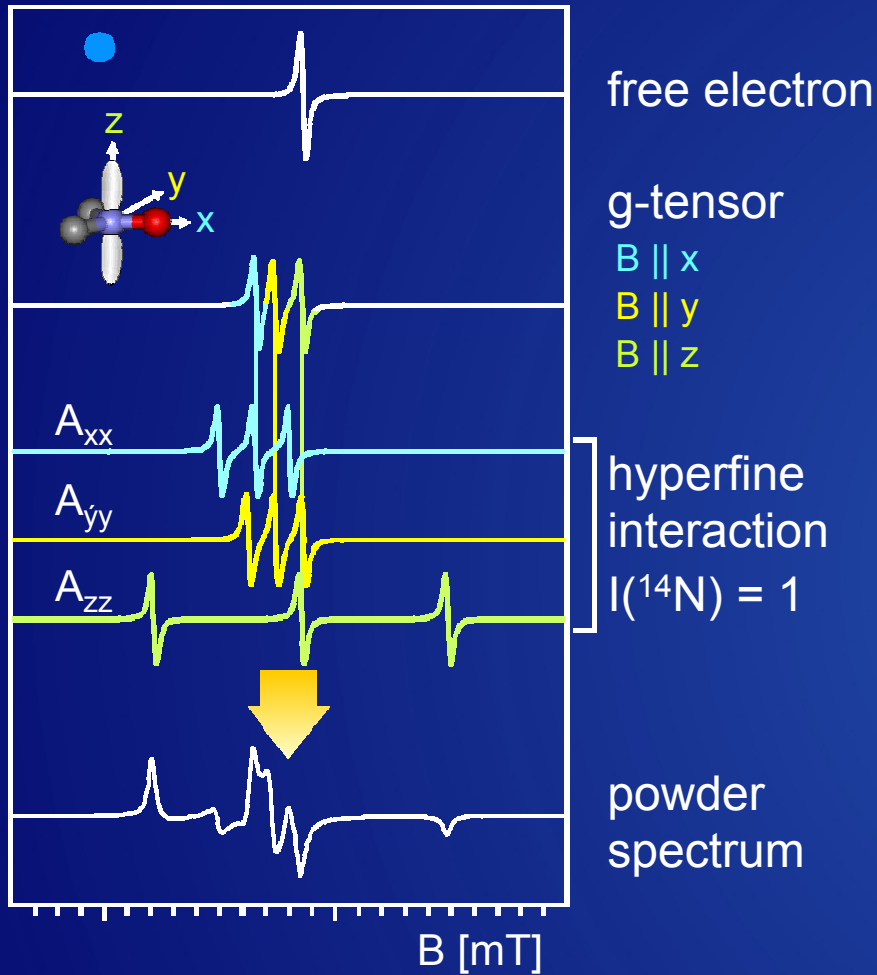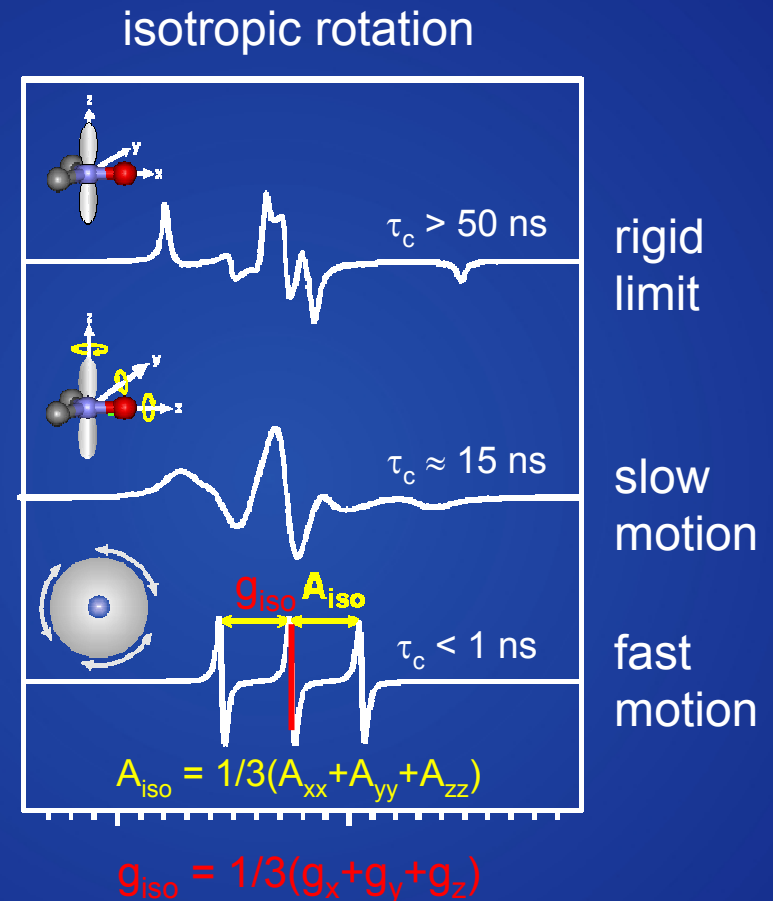
EPR spectroscopy

relaxation effects

system in thermodynamic equilibrium

non equilibrium situation

return to the thermodynamic equilibrium is characterized by two processes:

1. energy relaxation: spin lattice or longitudinal relaxation (T_1)
   no spontaneous emission at these frequencies; energy has to be transferred to some partner e.g. the solvent or the lattice in a solid

2. relaxation of the spin coherence: spin-spin or transversal relaxation (T_2) (entropic term)

ESR spectroscopy

relaxation mechanisms

fluid systems:

for a relaxation of an exited spin state one need fluctuating magnetic field. In particular, the fluctuating field should have a Fourier component at the resonance frequency.

Where do the fluctuating fields come from?

in fluids this comes mostly from rotational dynamics of the molecule or of parts of the molecule. This leads to fluctuating fields as long as there are anisotropic interactions.

The most efficient channel is usually the one arising form the interaction with the largest anisotropy:

- for systems with $S > \frac{1}{2}$: dipolar coupling between the spins
  (often this mechanism so fast that these systems cannot be observed in solution at all e.g. Ni^{2+}, Co^{2+})
- for $S = \frac{1}{2}$: for organic radicals often the anisotropic hyperfine
                 for transition metal ions often the anisotropic Zeeman interaction

an important channel is spin exchange with a fast relaxing agents (e.g. O_2)
(this is widely used and is called ESR oxymetry)

ESR spectroscopy

relaxation mechanisms

solid systems:

relaxation mostly mediated by lattice vibrations (phonons)
(coupling to the phonons via changes in the crystal field and spin orbit interaction)

two processes:

1. direct process (excitation or deexcitation of a phonon)
    longitudinal relaxation

    probability of this process depends on the density of states of the
    phonon spectrum at the given energy, thus it is temperature dependent

2. indirect process (Raman like process)
    second order process (just the difference between the two photons has
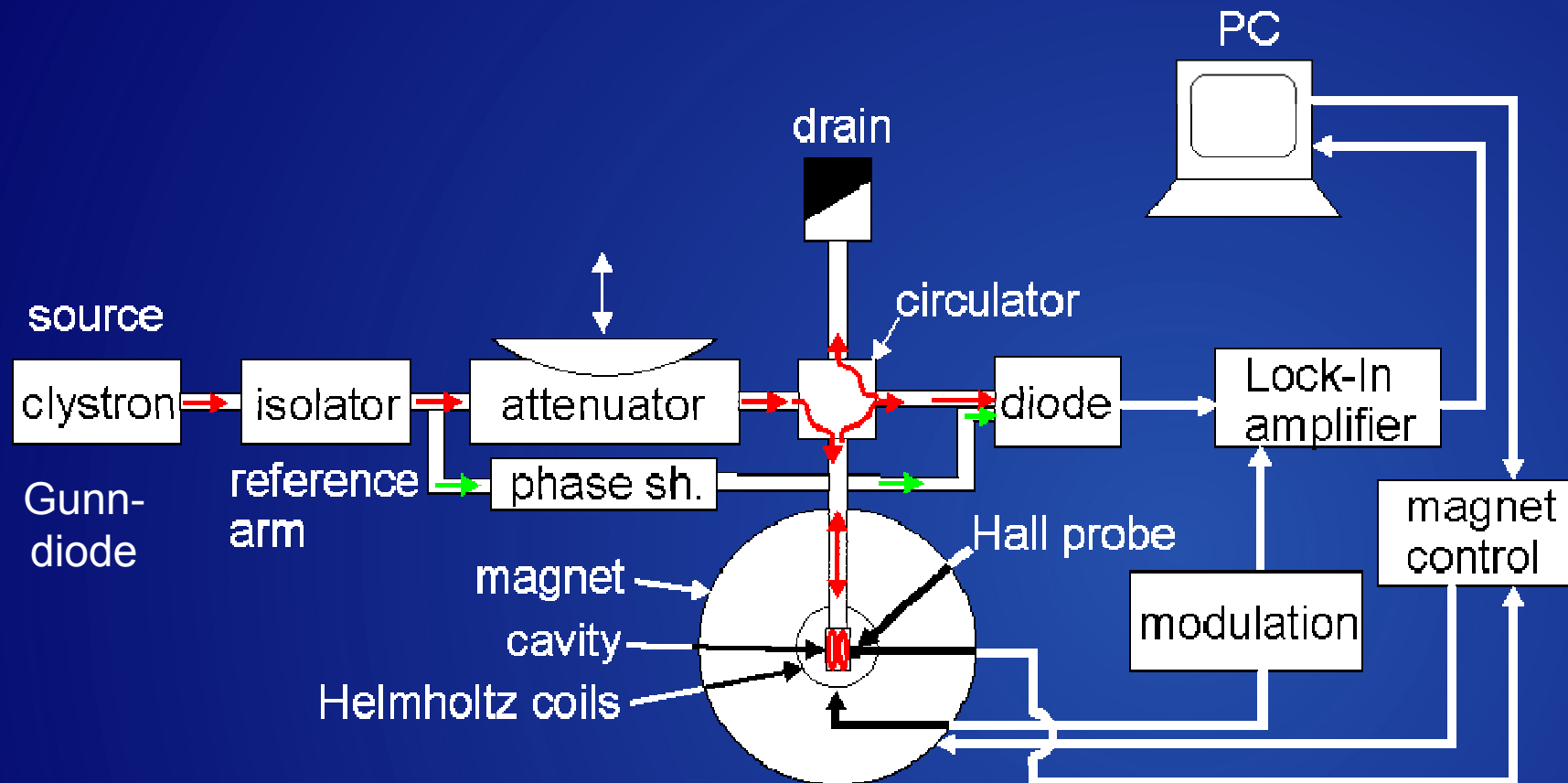   to match the energy of the excited spin state)

    The probability of such a process increases dramatically if real states
    are involved. This is particularly true for higher temperatures.

cw set-up at 10 GHz

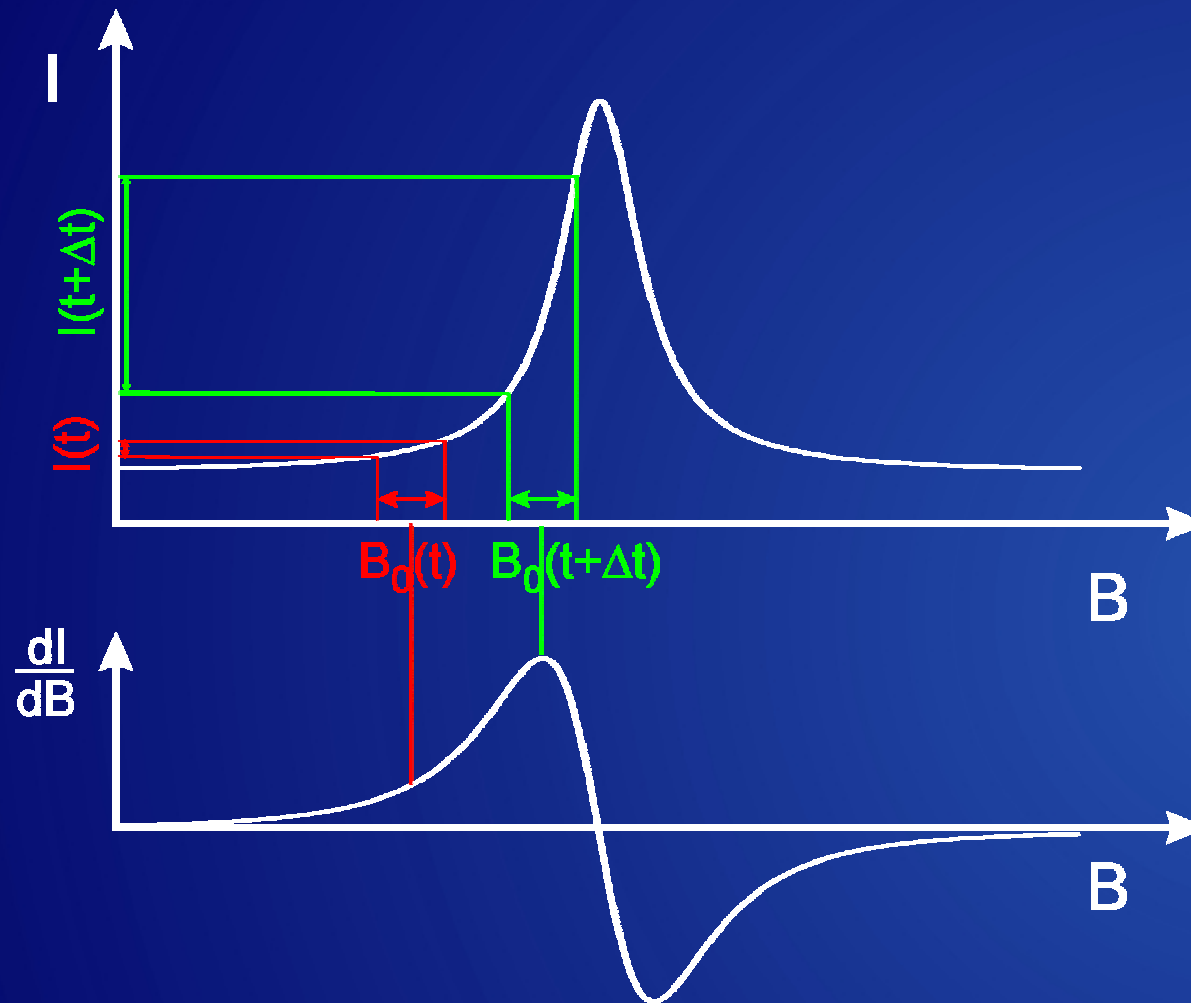# experimental aspects

consequence of lock-in detection
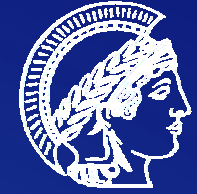
1. lock-in detection gives 1. derivative of the absorption line

2. holds only true if modulation amplitude is small as compared to line width
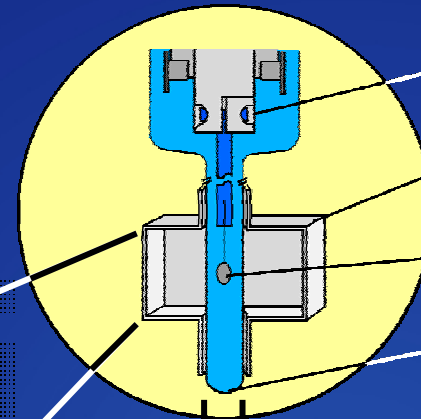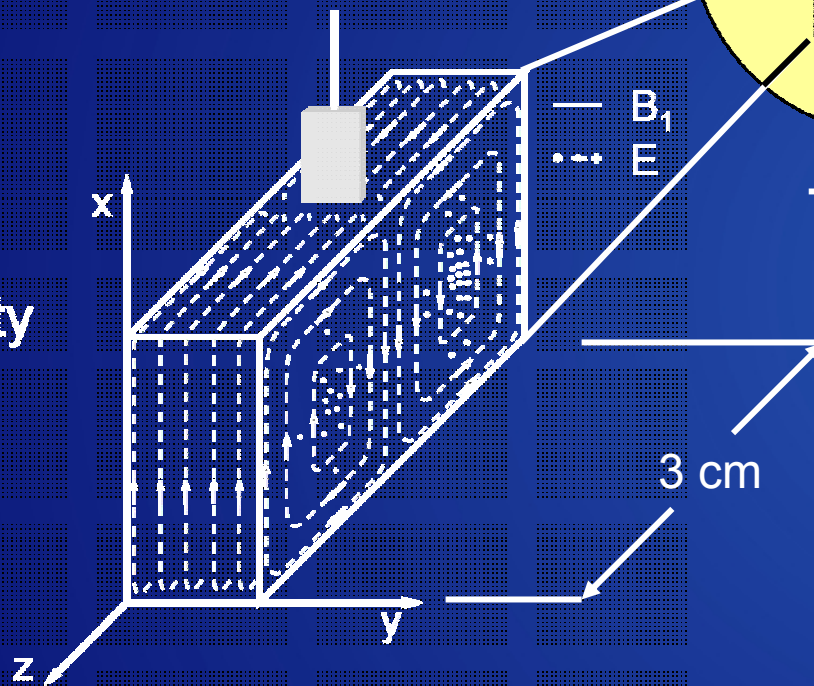
experimental aspects

resonators or cavities

field distribution in a microwave resonator

TE_{102}-cavity

helium cryostat
cavity
sample
quartz finger

1 cm

3 cm

B_1
E

x
y
z

experimental aspects

intensity of ESR spectra

What determines the signal intensity?

1. transition probabilities (calculated from quantum mechnics)

2. absorbed microwave power

$$\overline{P} = \frac{1}{2}\,\omega_0\,H_1^2\,\chi''$$

χ'' = complex part of the high frequency susceptibility

obeys Curie's law => I(ESR Signal) ~ 1/T

H_1 = oscillating magnetic field (perpendicular to the static magnetic field)
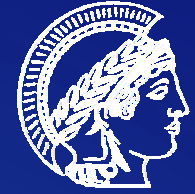
depends on the quality factor Q of the resonator

rectangular cavity:
$$H_1^2 = \frac{\mu H_0^2 Q_L (1 - \left|\Gamma_0\right|^2) P_{inc}}{4\pi\nu_0\mu'^2}$$

Γ_0: reflection coefficient

μ,μ': mag. perm. waveguide and cavity

experimental aspects

intensity of ESR spectra

What does this mean?

ESR is quantitative, but…

- relative numbers of spins in the sample: easy

- absolute numbers of spins in the sample: difficult

  (one needs a calibration standard which is measured under exactly the same conditions (including sample shape and size, temperature, microwave settings etc.)

- fraction of paramagnetic species as compared to the total number of species: very difficult

  only possible with detailed knowledge of the paramagnetic species (transition probabilities, relaxation properties, coupling situation) and an internal standard of known concentration

transition metal ions
electronic states and spin orbit coupling

We need the electronic ground state:

construction according to Hund's rules and Pauli principle

example: Co^{2+} ($3d^7$) for the ground state configuration see literature

$$l = \quad +2 \quad +1 \quad 0 \quad -1 \quad -2$$

↑↓	↑↓	↑	↑	↑

L = 3, S = 3/2 (assuming LS coupling)

$$^4F$$

no fields: degeneracy: (2S + 1)(2L + 1) = 28

if LS coupling is exactly correct: L = const. => $g = g_e$

spin orbit coupling lifts the degeneracy of states with equal L and S but different J

two contribution: 1. changes the splitting between states (m_S, m_{S+1}), shift of g_{iso}

2. depends on m_s^2 (only important for S > ½) no contribution to g_{iso}

often neither LS nor jj coupling correct. The correction to the LS case can be made by the so-called Racah coefficients B and C which are tabulated

transition metal ions
crystal or ligand field

no fields: degeneracy: $(2S + 1)(2L + 1)$

degeneracy is lifted partly by external electric fields

the external electric field can due to neighboring ions or ligands

lifting the degeneracy will lead to a partial decoupling of spin and orbit, thus the Racah coefficient are slightly small than in the free ion

drastic effects are observed if $\Delta > E_{pair}$

e_g

$S = 3/2$ $S = 1/2$

t_{2g}

high spin   low spin
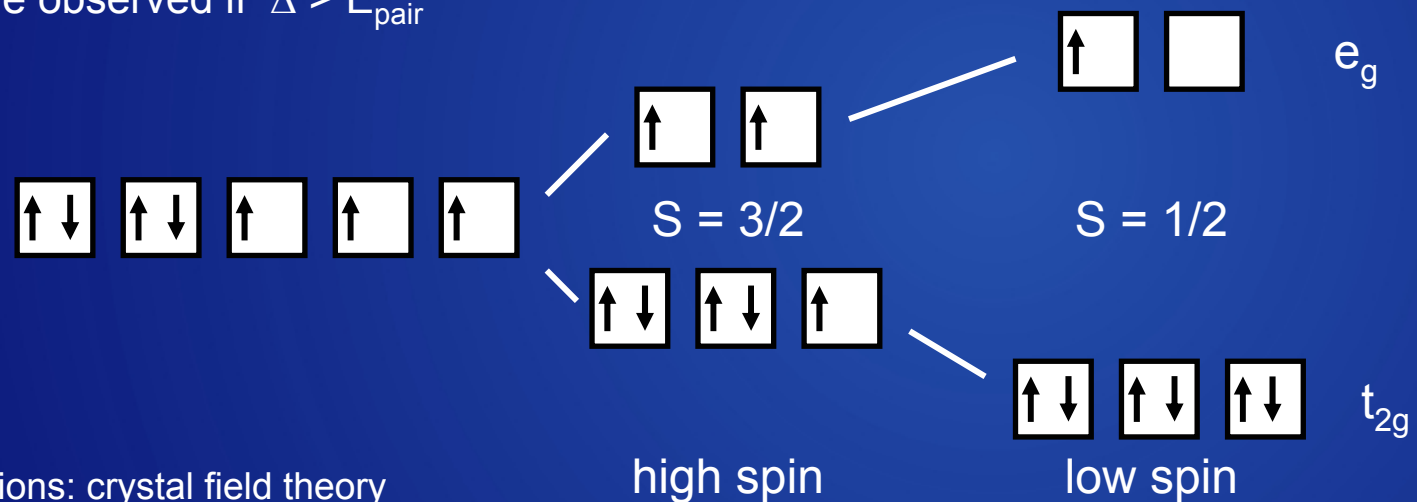
pure ionic interactions: crystal field theory

including covalency: ligand field, MO theory

transition metal ions

symmetry reduction

octahedral

spherical

e_g

t_{2g}

tetragonal

distortion

tetrahedral

t_{2g}

e_g

tetragonal

distortion

isotropic g, A   axial g, A
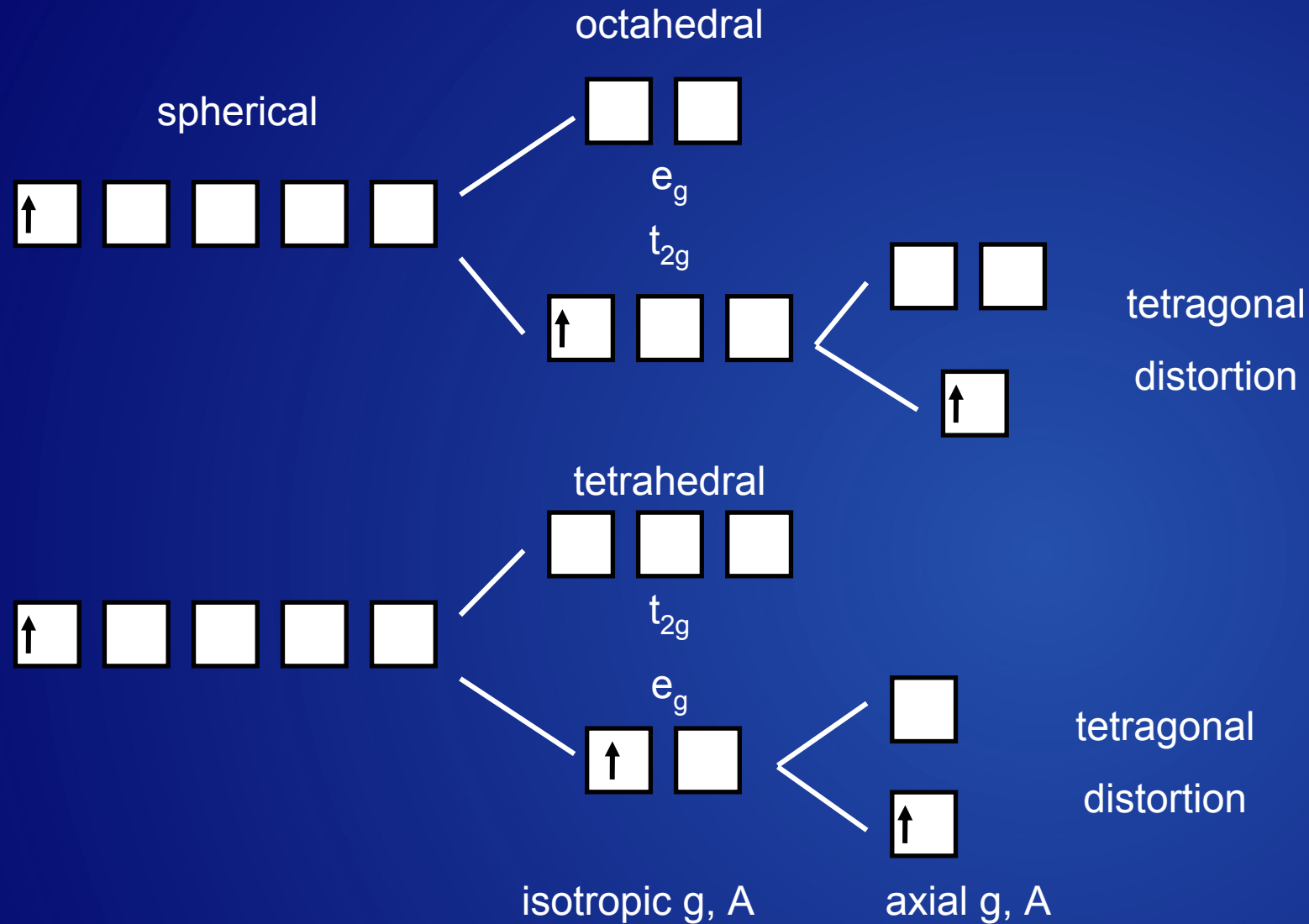
transition metal ions
Ti^{3+}, VO^{2+} (d^1)

Ti^{3+}:   typically 6 fold coordination in distorted octahedral symmetry

often axial symmetric tensor ($g_x = g_y \neq g_z$) g ≈ 1.85 - 2

87% of the isotopes have no nuclear moment

^{47}Ti (7.4 %; I=5/2) and ^{49}Ti (5.4%; I =7/2)

=> intense pattern due to g-anisotropy just weak satellites
     from hf-interaction

V^{4+}, VO^{2+}

isoelectronic to Ti^{3+}, mostly VO^{2+}

typical g-values: $g_{||}$ = 1.94, $g_\perp$ = 1.98-1.99

^{51}V (99.75%; I =7/2) => characteristic hyperfine pattern;
usually well resolved because of small g-tensor anisotropy

transition metal ions
Fe^{3+}, Mn^{2+} (d^5)

Fe^{3+}:   ground state ^6S, high-spin (S=3/2), low-spin (S=1/2)

in cubic symmetry: $g_{iso} \approx 2$

low symmetry: large zero-field splitting (only transitions within Kramers-Dubletts) large g-anisotropies $g_{||} = 2$, $g_{\perp} = 6$

97.8% of the isotopes have no nuclear moment
=> almost no hf-satallites

Mn^{2+} isoelectronic to Fe^{3+}; just high spin systems of importance

small g-anisotropy, much smaller zero-field splitting rf. Fe (a few GHz) transition between different Kramers multipletts possible

^{55}Mn (100%; I =5/2) => characteristic hyperfine pattern; usually well resolved because of small g-tensor anisotropy

transition metal ions
Co^{2+} (d^7)

Co^{2+}:   ground state ^4F, high-spin (S=3/2), low-spin (S=1/2)

octahedral and tetrahedral ligand field are usually distored

perfect octahedral symmetry: g_{iso} = 4.3

small distortion: g from 1.5 to 7; however, g_{iso} often close 4.3

in tetrahedral symmetry smaller deviations from g_e

low symmetry: large zero-field splitting (usually not possible to observe a spectrum in solution, require low temperatures)

^{59}Co (100%; I =7/2) => eight line spectrum

transition metal ions
Cu^{2+} (d^9)

Cu^{2+}:   ground state ^2D, S=1/2

usually distorted octahedral ligand field (tetragonal symm.)

=> axial symmetric tensor: g = 2 – 2.2; usually $g_{||} < g_{\perp}$

distorted tetrahedral ligand field (tetragonal symm.)

$g_{||} > g_{\perp}$ is usually found

^{63}Cu (69.2%; I =3/2); ^{65}Cu (30.8%; I =3/2);

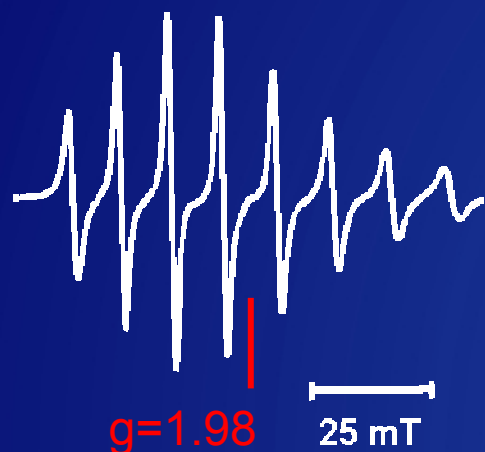almost equal gyromagnetic ratio => strongly overlapping

hyperfine multipletts
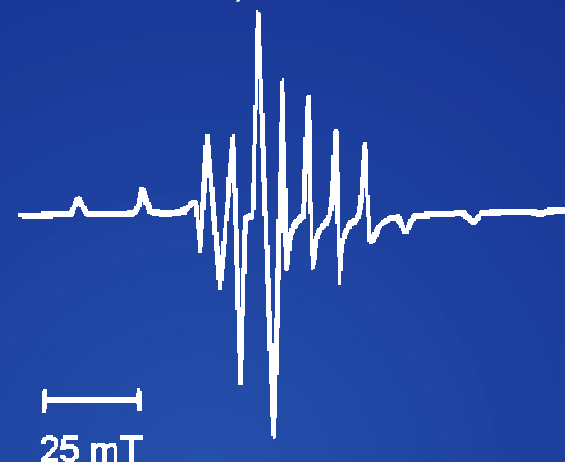
ESR spectroscopy

transition metal ions

Colloidal solution of nanoparticles
(in water at 300 K)

g=1.98   25 mT

 isotropic spectrum consist of 8 lines

=> hyperfine interaction: I = 7/2

no line in the center

=> all nuclei carry a spin of 7/2

three possibilities: ^{51}V, ^{59}Co, ^{181}Ta

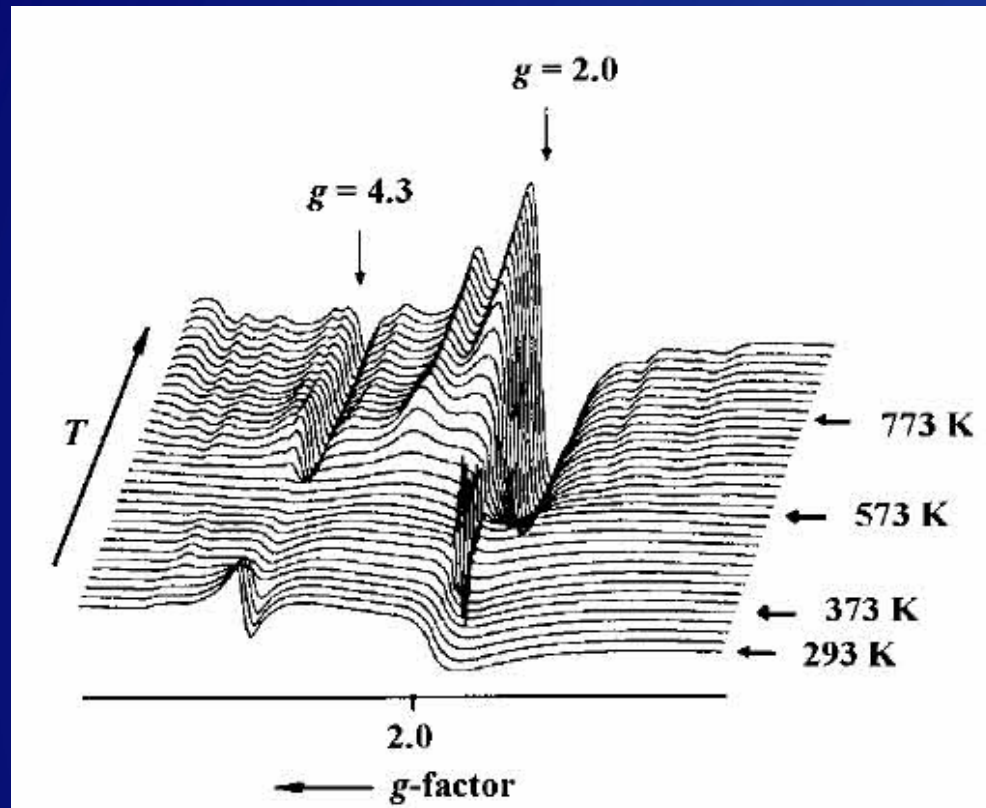Colloidal solution of nanoparticles
(in ice at 120 K)

25 mT

- moderate hyperfine anisotropy

($A_z \approx 20$ mT, $A_x = A_y \approx 8$ mT) $a_{iso} \approx 12$ mT

- almost isotropic g-value

$\Rightarrow$no Co;

Ta and V have similar electronic structures
however, the spin orbit coupling plays a much
bigger role for Ta.

ESR spectroscopy
transition metal ions

Fe in $AlPO_4$-5

two species: 1. g ≈ 2

2. g ≈ 4.3

1. species: octahedral coordinated Fe^{3+} on lattice positions

2. species: extra lattice Fe^{3+} in a distorted tetrahedral environment

strong redistribution of sites upon heating. At high temperature minimal 3 different sites occupied by Fe^{3+}. Regular lattice sites account for approx. 45% of the sites.
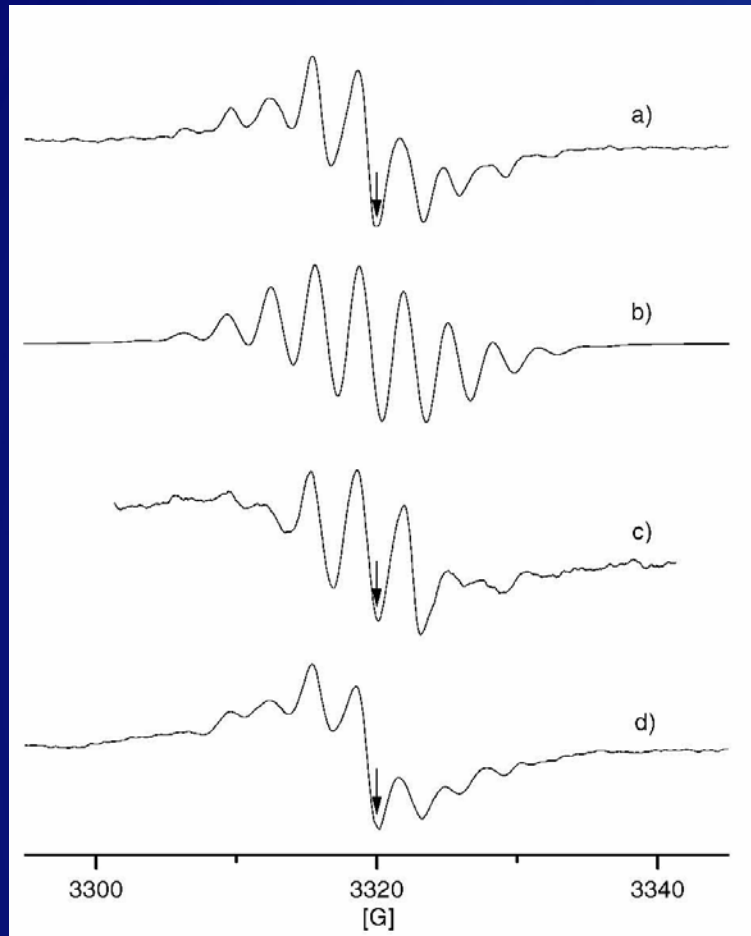
A. Brückner, U. Lohse, H. Mehner Microporous Mesoporous Mater. 20, 207 (1998).

ESR spectroscopy
transition metal ions

Benzene adsorbed to NaPdY(a), NaPtY (c) NaCeY (d) zeolithes

b) simulation assuming

$g_{iso} \approx 2.0023$

coupling to twelve equivalent protons

$a_{iso} = 0.312$ mT

Formation of benzene dimer radical cations

only isotropic values: due to fast motion

G. Hübner, E. Roduner Mag. Res. Chem. 37, S23 (1999).